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Growth and microhardness studies in solution-grown single crystals of thenardite

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Abstract : Single crystals of Thenardite (Sodium Sulphate Na_2SO_4) were grown by slow evaporation technique at room temperature. Mechanical characterization was done by Vickers microhardness testing. Load varying from 10 to 120 g was applied on selected (011) faces over a fixed interval of 10 seconds. Vickers hardness number (H_v) were found to decrease with increase in load. Meyer index 'n' was found to be less than 2 as expected and thus the particular crystal system belongs to soft material category. Neither Kick's law nor Hays and Kendall's law can satisfactorily explain the nonlinear variation of microhardness with load. Instead, it was best explained by Li and Bradt's Proportional Specimen Resistance (PSR) model. Crack lengths were measured and found to increase with load. The fracture toughness values (K_c) were estimated to be 0.227 and 0.151 MNm$^{-3/2}$ for (011) faces at 100 and 120 g respectively. The Brittleness indices (B_i) were determined as 1.455 and 3.297 nm$^{-1/2}$ respectively for the same faces at the same loads. Using Wooster's empirical relation, elastic stiffness coefficient, c_{11} has been calculated from hardness data.

Keywords : Thenardite, growth from solution, hardness, Meyer index, brittleness.

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1. Introduction

Hardness is an important property yielding knowledge about the strength of a material [1]. It is defined as the resistance it offers to the motion of dislocation, deformation or damage under an applied stress [2]. Stillwel [3] defined it as resistance against structural destruction. Plendl and Gielisse [4] have correlated the hardness of several crystals with lattice energy. Regarding mechanical properties, hardness testing provides useful information on the strength and the deformation characteristics of the materials and yield stress [5].

In recent years, Thenardite (Sodium Sulphate Na_2SO_4), an industrially rich chemical, finds application in detergent, glass, dyes, textiles, tanning and also in chemical industries. Moreover, salt cake (containing at least 97% Na_2SO_4) is used chiefly in wood digestion in pulp and paper industry. Sodium Sulphate (SS) is one of the main constituents of natural brine. It can crystallize in at least five different forms [6]. In the temperature below 185°C of Na_2SO_4, form V becomes stable and it corresponds to Thenardite (anhydrous Sodium Sulphate) and crystallizes in an orthorhombic lattice having space group F_{DDD} with a_0 = 5.863Å, b_0 = 12.304 Å, c_0 = 9.82 Å and Z = 8 [7]. Thenardite is actually the dehydration product of mirabilite or Glauber's Salt $Na_2SO_4.10H_2O$ [8].

Single crystals have found application in various branches of science and technology owing to their unique physical properties. In continuation of our earlier woks on pure ADP, pure KDP [9], mixed ADP-KDP [10], pure Ammonium Sulphate (AS) [11] and mixed Ammonium-Potassium Sulphate (AS-PS) [12], we will present here the recent results on mechanical properties on solution-grown single crystals of Sodium Sulphate (Na_2SO_4).

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2. Experimental

Single crystals of SS were grown at an ambient temperature of 34°C by slow evaporation technique from the supersaturated solution of the same. Transparent crystals having typical growth morphology were found at different pH values.

Mechanical characterization of the SS system was done by microhardness testing. The microhardness of the above crystals was performed using mhp 160 microhardness tester fitted with Vickers diamond pyramid indentor and attached to Carl-Zeiss (Jenavert) incident ray microscope. SS crystals with flat smooth (011) faces were selected for indentation studies. For static indentation test, loads varying from 10 to 120 g were applied on selected faces for a dwell period of 10 sec. Several indentations were made for each load and the averages of the diagonals of at least 5 impressions were recorded using a calibrated micrometer attached to the eyepiece of the microscope. Vickers microhardness numbers (H_v) were calculated using the standard formula

$$H_v = 1.8544\, P/d^2, \quad (1)$$

where P is the applied load in kg, d is average diagonal length in mm and H_v is in kg/mm^2.

Crack length was measured from the centre of indentation mark to the crack end. Crack length can be measured from 70 to 120 g.

Resistance to fracture indicates the toughness of a material [13]. The fracture mechanics of the indentation process gives an equilibrium relation for a well-developed crack extending under the centre loading condition

$$P/l^{3/2} = B_0 K_c, \quad l \geq d/2, \quad (2a)$$

where l is the average of two crack lengths for each indentation, B_0 is the indentor constant, equal to 7 for Vickers diamond pyramid indentor [14] and the other symbols have their usual meanings.

Brittleness is a special property of a brittle material affecting the mechanical behaviour of it and can be expressed in terms of brittleness indices (B_i) as

$$B_i = H_v / K_c \, . \quad (2b)$$

The elastic stiffness coefficient c_{11} is defined as the ratio of stretching force parallel to X_1 axis to the expansion in that direction when a crystal is stretched simultaneously with unequal forces in all the three directions so that uniform expansion parallel to X_1 axis takes place. Wooster [15] has established an empirical relation ($c_{11} = H^{7/4}$) between elastic stiffness constant (c_{11}) and hardness of a material. This relation has been used to calculate the value of c_{11} for SS system.

3. Results and discussion

Figure 1(a) illustrates the indentation mark on (011) faces of SS at 20 g of load. Figure 1(b) shows the picture of indentation impression (produced by 100 g of load) that

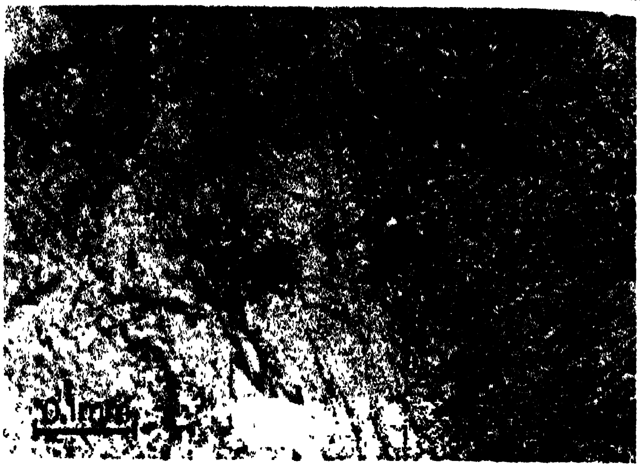

Figure 1(b). Indentation impression after nearly 1 week of its production by a load of 100 g.

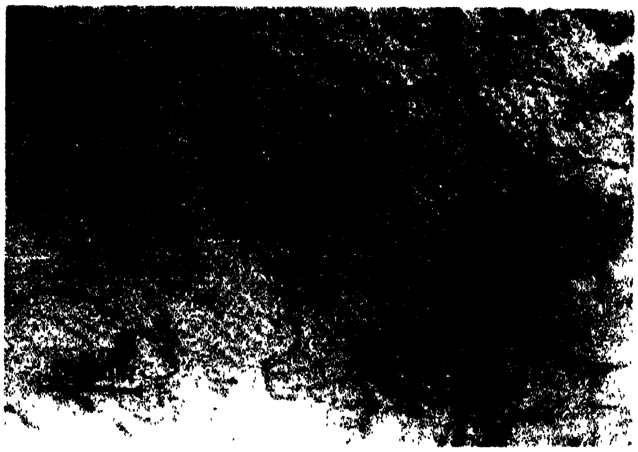

Figure 1(a). Indentation mark on (011) faces of SS at 20 g of load

was taken after the load was released for nearly 1 week. With gradual increase of the applied stress on a material, the elastic limit can be exceeded and the specimen will not restore to its original shape on the removal of the stress [9], which is very much evident from Figure 1(b). The values of H_v calculated using eq. (1) for various loads were plotted against loads (Figure 2). It is clear from the figure that Vickers microhadness numbers (H_v) decrease with increase in loads. In the low load region (LLR) indentor penetrates only the surface layer and hence its effect is responsible for the sharp decrease in H_v in this region (between 10 to 40 g). The penetration depth further increases with increase in loads and in the intermediate load region (ILR) the overall effect is due to both surface and inner layers [16]. This mixed effect is responsible for the non-linear variation of H_v in the ILR (between 40 to 70 g). Here the fall of H_v with load is not so sharp and tries to attain saturation. With further increase in load in the higher load region (HLR), the effect of the inner layers become more and more prominent. Moreover, for brittle materials it is observed that

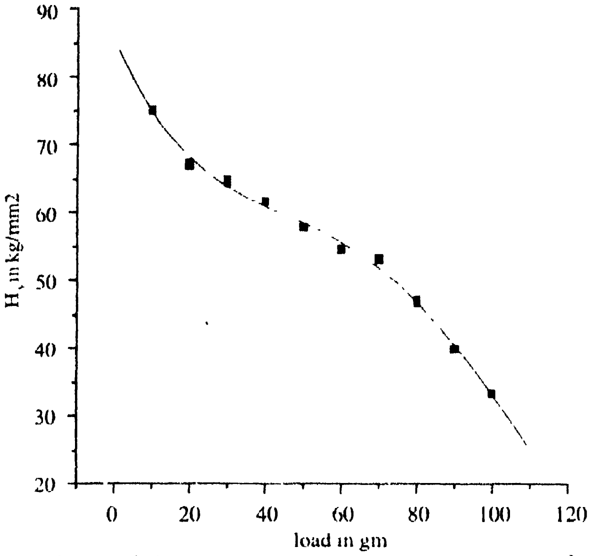

Figure 2. Plot of Vickers microhardness number (H_v) in kg/mm^2 against load (P) in g.

with increase in Vickers indentor load, there is a possibility of transition from purely inelastic deformation to the formation of well defined cracks across the major diagonals of the Vickers indentor, which are extended due to subsequent loading [17]. In our case of SS, cracking starts at nearly 70 g of the indentation load. Thus in SS system, cracking effect may be predominant and for this we do not get saturation of H_v in HLR (beyond 70 g) (Figure 2), though in very few cases saturation is obtained at higher loads (not shown in the figure) due to the prominent effect of inner layers. The observed phenomenon of dependence of microhardness of a solid on the applied load at low level of testing load is known as indentation size effect (ISE). The observed decrease in microhardness with increasing load is termed as normal ISE, which was also observed earlier by several other workers [9, 18–24]. Maximum indentor load applied for SS was 120 g beyond which microcracks were observed around the indentation mark.

The errors on H_v were estimated for each P/d^2 using the formula

$$\Delta H_v = 1.8544[\{(1/y)\,\Delta P\}^2 + P^2/y^4\,(\Delta y)^2]^{1/2} \tag{3}$$

where $y = d^2$ and $\Delta y = 2d\Delta d$, ΔP is the experimental error on P [13]. The average error on the measurement of microhardness ΔH_v was found to be ± 4.7 g/µm^2.

The relation between load and the size of indentation can be expressed by Meyer's law [25] as

$$P = k_1 d^n, \tag{4}$$

where k_1 is the material constant (standard hardness), n is the Meyer index and other symbols have their usual meanings. Figure 3, illustrating the plot of log P against log d for SS, is in good agreement with Meyer's law.

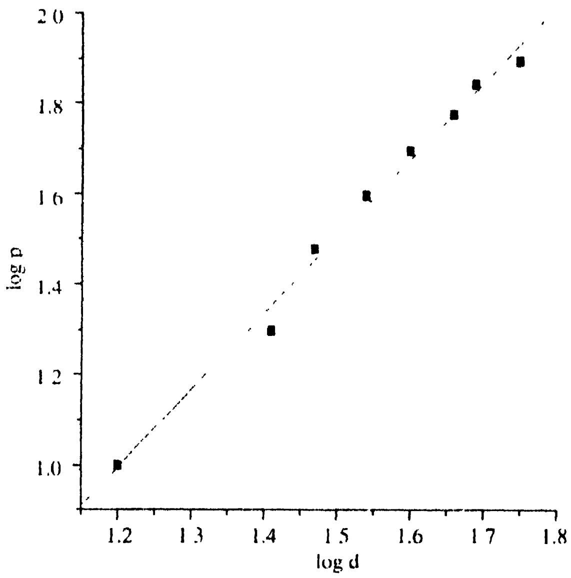

Figure 3. Plot of log P against log d (P in g, d in µm).

The value of n, calculated using least square fitting method was found to be 1.75. Combining eqs. (1) and (4) we get

$$H_v = bP^{(n-2)/n} \tag{5}$$

Here b is a new constant. This expression shows that H_v should increase with increase in P if $n > 2$ and decrease with increase in P if $n < 2$. This is in good agreement with the experimental data and hence normal ISE. According to Onitsch [26] and Hanneman [27], n should lie between 1 to 1.6 for hard materials and above 1.6 for softer ones. Thus our crystal belongs to soft material category.

Now, we will try to explain the observed variation of hardness with load more explicitly by Hays and Kendall's law [28]. According to this law, there is a minimum level of indentation load, W (known as resistance pressure), to cause an indentation. Below this, no plastic deformation occurs, but elastic deformation can occur. Hays and Kendall have modified Kick's law ($P = k_2 d^2$) [29] and proposed their theory of resistance pressure as

$$P - W = k_2\, d^2, \tag{6a}$$

which, can be rearranged as

$$P = W + k_2\, d^2, \tag{6b}$$

where k_2 is a constant, $n = 2$ is the logarithmic index. The plot of P against d^2 (Figure 4) is a straight line and the slope gives the constant k_2 (equals to 0.025 x 10^{-3} kg). Combining eqs. (4) and (6), we have

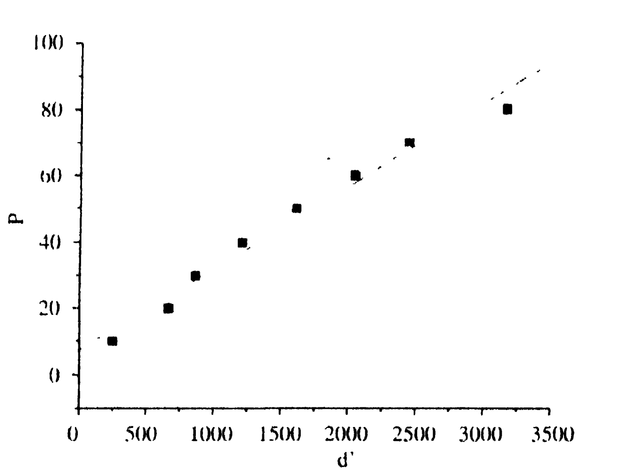

Figure 4. Plot of P *versus* d^2 (P in g, d in μm).

$$W = k_1\, d^n - k_2\, d^2$$

or $$d^n = W/k_1 + k_2/k_1\, d^2, \qquad (7)$$

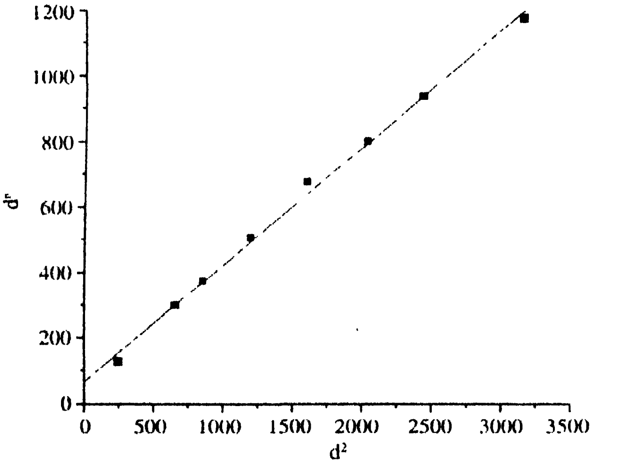

Figure 5. Plot of d^n against d^2 (d in μm).

The plot of d^n *versus* d^2 (Figure 5) is a straight line yielding slope k_2/k_1 and the intercept W/k_1 from which we have calculated W (equals to 4.88 g). Because the value of W have now been determined, this point can be examined well by taking logarithmic of equation (6a) as

$$\log\,(P-W) = \log k_2 + n_w \log d \qquad (8)$$

where subscript w is applied to the exponent to relate it to the calculation of W [30]. If the ISE is from the sample resistance W to initiate plastic deformation then the plot of log (P-W) *versus* log d should yield n_w equal to 2. But our plot of the same with experimentally obtained data (Figure 6) yielding n_w equals to 2.17. This is not equal to 2 and significantly different from the power law exponent of eq. (4), summarized in Table 1. Moreover, the calculated W is large with respect to the load at which the initiation of plastic deformation occurs. This suggests that ISE cannot be explained simply by taking the deformation initiation resistance W into account.

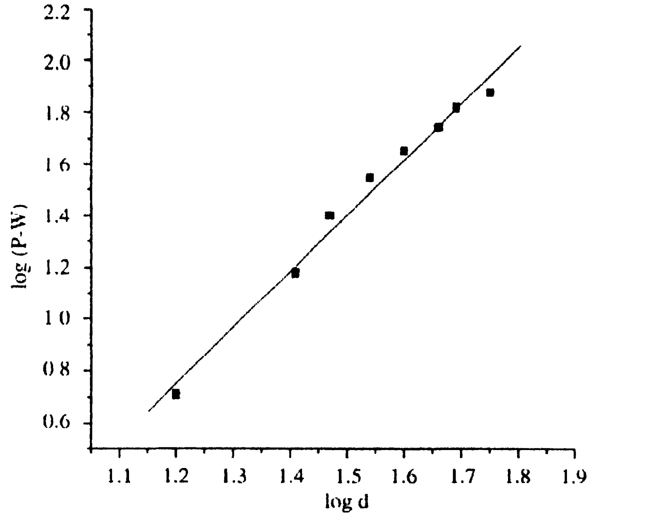

Figure 6. Changes of log (P-W) as a function of log d (P and W in g, d in μm).

Recently, Li and Bradt [31] have tried to explain the ISE with the help of their general Proportional Specimen Resistance (PSR) model. According to PSR model, the

Table 1. Calculated values of n, W and n_w for thenardite crystal.

n (from Meyer's law)	k_1 (10^{-3} kg)	W/k_1	k_2/k_1	k_2 (10^{-3} kg)	W (10^{-3} kg)	n_w (from Hays and Kendall's law)
1.75	0.076	64.03	0.357	0.027	4.88	2.17

observed decrease in microhardness with load is dependent on two factors : (i) the frictional force between the test specimen and the indentor facets and (ii) the elastic resistance of the test specimen. In PSR model, microhardness has two distinct parts : (i) the indentation load-dependent, ISE regime; and (ii) the indentation load-independent regime [32]. Here indentation test load P is related to the indentation size (d) as

$$P = a_1\, d + a_2\, d^2, \qquad (9)$$

where a_1 coefficient is the PSR contribution to the apparent microhardness and is related to the power-law exponent, the n value. The term a_2 is not related to ISE. Rather, it relates to the load-independent microhardness and is equal to P_0/d_0^2 [30]. Here, P_0 is the critical applied indentation load above which the hardness becomes independent of the applied load and d_0 is the corresponding indentation size. Eq. (9) can be rearranged as

$$P/d = a_1 + (P_0/d_0^2)\, d \qquad (10)$$

i.e., a plot of P/d against d should be a straight line, the slope of which gives the value of load independent microhardness. Applying PSR model of Li and Bradt in case of Sodium Sulphate, it has been observed that a plot

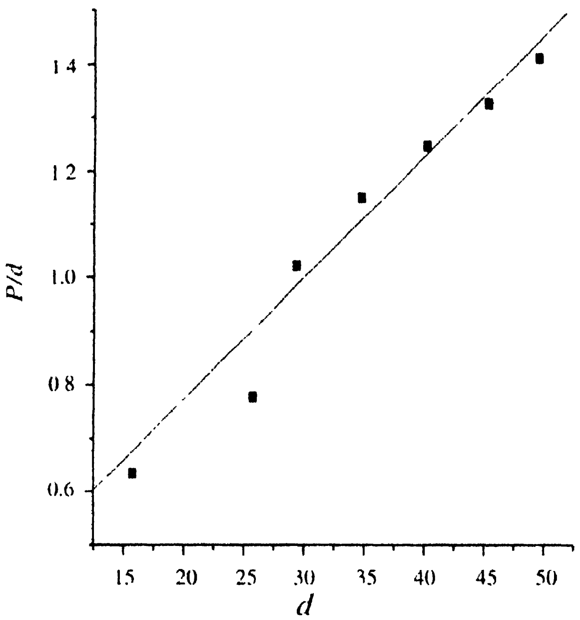

Figure 7. Plot of P/d against d (P in d, d in μm).

of P/d against d gave a straight line (Figure 7). This linear relation confirms that PSR model is also applicable in our SS system. The slope of the straight line curve (P_0/d_0^2) multiplied by the Vickers conversion factor 1.8544 gives load-independent hardness number and it was turned out to be 42.33 kg/mm^2. The value of a_1 is 0.311 kg/mm.

Fracture toughness (K_c) was calculated using eq. (2a). The values of K_c turned out to be 0.227 and 0.151 MNm$^{-3/2}$ at 100 and 120 g respectively, for (011) faces of SS crystals.

The values of Brittleness index (Bi), estimated from eq. (2b), were found to be 1.455 and 3.297 μm$^{-1/2}$ at 100 and 120 g respectively, for (011) faces of SS crystals.

We have calculated the value of c_{11} (actually the averages of c_{11}, c_{22} and c_{33} for an orthorhombic system) using Wooster's empirical relation as 0.434 x 10^{12} c.g.s. units. We cannot compare it, as no standard data is available for SS system. All the calculated values of l, K_c, Bi and c_{11} are tabulated in Table 2.

Table 2. Calculated values of l, K_c, B_i and c_{11} for thenardite crystal.

l μm	K_c MNm$^{-3/2}$	B_i μm$^{-1/2}$	c_{11} (c.g.s. units)
51 at 70 g	0.227 at 100 g	1.455 at 100 g	0.434 x 10^{12}
74 at 90 g	0.151 at 120 g	3.297 at 120 g	
73 at 100 g			
107 at 120 g			

4. Conclusions

From the overall studies of microhardness in solution grown single crystals of Thenardite (SS), it can be concluded that Vickers microhardness value H_v is in the range 75-35 kg/mm^2 for (011) faces under an applied load in the region 10–100 g. This decrease in H_v with load is in good agreement with the theoretical prediction by Onistch [26] and Hanneman [27]. The observed nature of H_v with load is discussed in terms of surface and inner layer effect and also by the effect of cracking at higher loads.

The variation of Vickers microhardness follows the normal ISE trend *i.e.*, decrease in H_v with load. The value of Meyer index (n) is always less than two. Thus SS falls in the soft material category and it confirms that Meyer's relationship also holds for the ISE of the Vickers microhardness of SS to a certain value of load.

By applying Hays and Kendall's law [28], the materials resistance pressure (W) has been calculated and it turned out to be 4.88 (10^{-3} kg).

A proportional specimen resistance (PSR) model was applied to explain the ISE. It has been confirmed that the ISE is the result of PSR, which is composed of (i) the elastic resistance of the test specimen and (ii) the friction at the indentor facet/specimen interface. The n value of the power law was confirmed to be directly related to the a_1 value of the PSR model. The second coefficient a_2 is not related to ISE. Rather, it can be related to load-independent hardness or true hardness. The value of load-independent hardness is 42.33 kg/mm^2.

We have also calculated the value of c_{11} for SS system. The value of c_{11} gives an idea of tightness of bonding between neighbouring atoms. The value of c_{11} for SS is 0.434 x 10^{12} c.g.s. units. We cannot compare this value, as no standard data is available. However, it may be noted that it is lower than that of PS but greater than AS. This indicates that the binding force between Na^+ and $SO_4^=$ is stronger than that between NH_4^+ and $SO_4^=$ but weaker between K^+ and $SO_4^=$ [11]. The hardness measurement is therefore, useful in indicating the order of magnitude to be expected for the elastic constant in a new material.

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